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<b>(21) International Application Number:</b> PCT/EP97/00892  <b>(22) International Filing Date:</b> 21 February 1997 (21.02.97)  <b>(30) Priority Data:</b> 1002427 23 February 1996 (23.02.96) NL  <b>(71) Applicant:</b> AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).  <b>(72) Inventors:</b> VAN DEN BERG, Keimpe, Jan; Venus 173, NL-6922 LZ Duiven (NL). HOBEL, Klaus; Saarlandstrasse 12, D-63906 Erlenbach (DE). KLINKENBERG, Huig; Noordeinde 23, NL-2225 CS Katwijk aan Zee (NL). NOOMEN, Arie; Dillestraat 27, NL-2215 BM Voorhout (NL). VAN OORSCHOT, Josephus, Christiaan; Johannes Rutgersstraat 19, NL-6936 HH Arnhem (NL).  <b>(74) Agent:</b> SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).	<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> COATING COMPOSITION COMPRISING A BICYCLO- OR SPIRO-ORTHOESTER-FUNCTIONAL COMPOUND  <b>(57) Abstract</b>  The invention pertains to a coating composition comprising a first compound comprising at least one bicyclo- or spiro-orthoester group and a second compound comprising at least two hydroxyl-reactive groups. The invention also comprises a process for curing the present coating composition. More particularly, the latent hydroxyl groups of the bicyclo- or spiro-orthoester groups have to be deblocked and reacted with the hydroxyl-reactive groups of the second compound if the present coating composition is to be cured. Further, a process for making bicyclo-orthoester compounds from the corresponding oxetane compound is described, as are polymers comprising at least one bicyclo- or spiro-orthoester group.		

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# COATING COMPOSITION COMPRISING A BICYCLO- OR SPIRO-ORTHOESTER-FUNCTIONAL COMPOUND

- 5 The invention pertains to a coating composition comprising a first compound comprising at least one bicyclo- or spiro-orthoester group.

The use of compounds comprising bicyclo-orthoester groups in coating compositions is known from US patent publication No. 4,338,240. In this  
10 patent publication the use and the preparation of bicyclo-orthoester-functional compounds (hereinafter bicyclo-orthoester will be abbreviated to BOE) is described. Described are, e.g., BOE-functional compounds, which are the adduct of two compounds comprising one hydroxyl group and one BOE group and one compound comprising two isocyanate groups. The  
15 compounds are cross-linked by means of cationic ring opening homopolymerisation of the BOE groups. In that case, however, the presence of moisture has to be excluded. Furthermore, energy in the form of ultraviolet, infrared or microwave irradiation or heat has to be supplied during the polymerisation process.

20 The invention now provides a coating composition of the aforementioned type which is free of said drawbacks. For that reason the coating composition mentioned in the opening paragraph is characterised in that it comprises a second compound comprising at least two hydroxyl-reactive  
25 groups.

A coating composition comprising a compound comprising at least one bicyclo- or spiro-orthoester group (hereinafter spiro-orthoester will be abbreviated to SOE) is a composition having latent hydroxyl groups. In the  
30 presence of water or moisture from the air the BOE or SOE groups will be hydrolysed, forming hydroxyl groups. This reaction is also known as deblocking. During deblocking few if any volatile components are released.

When the BOE- or SOE-group is deblocked in this manner, it is not possible to obtain a homopolymer of BOE- or SOE groups by cationic polymerization. However, it has now been found that when a second compound comprising at least two hydroxyl-reactive groups is present in the composition, the deblocked hydroxyl groups can react with the hydroxyl-reactive groups to give a cross-linked polymer.

BOE- and SOE-functional compounds may be used as main binders or as reactive diluents in the coating compositions of the present invention.

10 The use of compounds comprising BOE or SOE groups in coating compositions has several advantages over the use of compounds having free hydroxyl groups, such as hydroxyl-functional reactive diluents, hydroxyl-functional main binders, e.g. polyester polyols and acrylate polyols, and even compounds where the BOE or SOE groups have already been hydrolysed.

20 Firstly, the viscosity of compounds comprising BOE or SOE groups is lower than that of the corresponding hydrolysed compounds. In consequence, less viscosity-reducing solvent which evaporates in air is needed in the coating composition.

25 Secondly, because of the stability of the BOE- and SOE-functional compounds the pot life:drying time ratio of compositions according to the invention is particularly favourable, for hydrolysis only takes place in the presence of water or moisture.

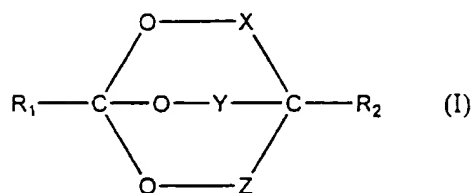
Thirdly, in coating compositions of the present invention BOE- and SOE-functional compounds have the advantage that hydrolysis of the BOE or

SOE group produces a substantial increase in the composition's viscosity. A high viscosity will give reduced sagging of the coating composition on the substrate.

- 5 Finally, it has been found that the coating compositions of the present invention provide a high build behavior.

By BOE groups are meant in this connection groups having a structure according to formula I

10



wherein

- 15 X and Z are independently from each other selected from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

Y is nothing or is selected independently of X and Z from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

- 20 R<sub>1</sub> and R<sub>2</sub> may be the same or different and are selected from the group of monovalent radicals comprising

- hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen,  
 25 sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus,

sulphoxy, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and divalent radicals comprising

alk(en)ylene groups having 1-10 carbon atoms which groups may be linear  
 5 or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphony, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl,  
 10 and acyl groups, ester groups; ether groups; amide groups; thioester groups; thioamide groups; urethane groups; urea groups; and a single bond.

Preferably, X, Y, and Z are methylene. R<sub>1</sub> and R<sub>2</sub> in that case are linked to  
 15 a divalent 2,6,7-trioxabicyclo[2.2.2]octane radical.

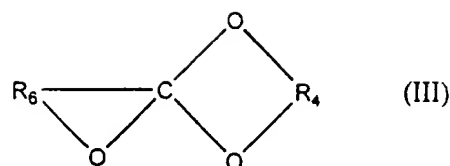
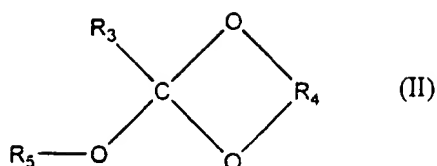
In the case of R<sub>1</sub> and R<sub>2</sub> being both monovalent radicals, the BOE group as defined by formula I is the same as the BOE-functional compound. Monovalent radicals R<sub>1</sub> and R<sub>2</sub> are preferably independently from each  
 20 other selected from the group of hydrogen, hydroxyl, and linear or branched alk(en)yl groups having 1-20 carbon atoms, optionally substituted with one or more hydroxyl groups and optionally comprising an ester group. Examples of such groups are: methyl, methylol, ethyl, ethylol, propyl, propylol, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, a -CH<sub>2</sub> -  
 25 CH<sub>2</sub> - O - CO - C<sub>1-20</sub> alk(en)yl group, and mixtures thereof.

Preferably, R<sub>1</sub> is linear or branched alk(en)yl having 1-20 carbon atoms, optionally substituted with hydroxyl, while R<sub>2</sub> is methyl or ethyl. Alternatively, R<sub>1</sub> can be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl,

octyl, nonyl, decyl, undecyl, and mixtures thereof, while  $R_2$  can be methylol, ethyl, ethylol or a  $-CH_2-CH_2-O-CO-C_{1-20}$  alk(en)yl group.

- When a divalent radical is selected for either or both  $R_1$  or  $R_2$  groups, high-molecular weight BOE-functional compounds can be formed. These may be adducts or polymers comprising several BOE groups. Thus two BOE groups can form an adduct by selecting a monovalent radical for one of the two  $R_1$  and  $R_2$  groups, and a divalent radical for the other. The BOE groups will then be linked together via the divalent radical. BOE groups may also be linked via the divalent radicals to monomer or oligomer compounds. Such BOE-functional compounds are, e.g. described in above-mentioned US 4,338,240. For example, two BOE groups may be linked to a dimer fatty acid, e.g. Pripol 1009, ex. Unichema. Alternatively, in the aforementioned configuration the BOE groups can function as side groups or terminal groups in a polymer chain. The polymers can be, e.g., polyesters, polyethers, polyacrylates, polyamides or polyurethanes. When the divalent radical is a single bond, the BOE group is bonded directly to the polymer. When the  $R_1$  and  $R_2$  groups are both divalent, the BOE groups can be incorporated into the main chain of a polymer or they can serve to link two polymer chains together. Preferably, one or both  $R_1$  and  $R_2$  groups are selected from the group of ester, ether, urethane, a single bond, and alk(en)ylene groups having 1-10 carbon atoms which may be linear or branched and may contain one or more ester, ether, or urethane groups.
- The term SOE groups in this case refers to groups having a structure according to formula II or III

6



wherein

5  $R_3$  and  $R_5$  are independently from each other selected from the group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and

10  $R_4$  and  $R_6$  are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals

such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and

divalent radicals

15 such as a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.

20 Preferably,  $R_3$  and  $R_5$  are selected independently from linear or branched alk(en)yl groups having 1-4 carbon atoms, e.g., a methyl or ethyl group.

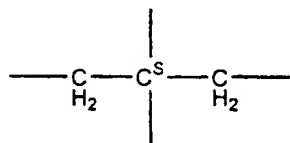
In the case that neither of  $R_4$  and  $R_6$  is substituted with a divalent radical, the SOE group as defined by formulae II and III is the same as the SOE-  
25 functional compound.



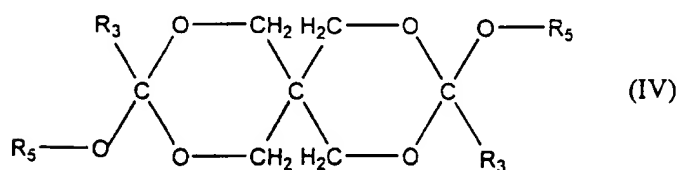
When a divalent radical is selected as substituent for either or both  $R_4$  and  $R_6$  groups, high-molecular weight SOE-functional compounds can be prepared in the same manner as described above for high-molecular BOE compounds. When  $R_4$  or  $R_6$  has one divalent radical substituent, adducts or polymers can be made which have SOE groups as terminal or side groups. In formula III,  $R_4$  and  $R_6$  can both have divalent radicals as substituents, in which case the SOE group can be incorporated into the main chain. The polymers may be, e.g., polyacrylate, polyester, polyether, polyamide or polyurethane.

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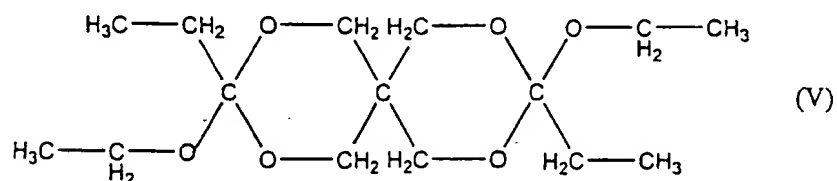
Alternatively,  $R_4$  can be



15 with the compound formed being point symmetrical to  $C^S$ , giving a SOE compound according to formula IV:



20 Preferably, formula IV is:



Preferably,  $R_4$  is ethylene, optionally substituted with a linear or branched alkyl group having 1-5 carbon atoms, optionally containing one or more oxygen and nitrogen atoms. For instance,  $R_4$  may be:



Preferably,  $R_6$  is propylene.

10 In addition to the BOE- or SOE-functional compound the coating composition according to the invention comprises a second compound comprising at least two hydroxyl-reactive groups. The hydroxyl-reactive groups are selected from the group of isocyanate, epoxy, acetal, carboxyl, anhydride, and alkoxy silane groups. Also, mixtures of these groups in one compound are included. Alternatively, the second compound can be an amino resin.

15

Examples of compounds comprising at least two isocyanate groups are aliphatic, alicyclic, and aromatic polyisocyanates such as trimethylene diisocyanate, 1,2-propylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate,  $\alpha,\alpha'$ -dipropyl ether diisocyanate, 1,3-cyclopentylene diisocyanate, 1,2-cyclohexylene diisocyanate, 1,4-cyclohexylene diisocyanate, 4-methyl-1,3-cyclohexylene diisocyanate, 4,4'-dicyclohexylene diisocyanate methane, 3,3'-dimethyl-4,4'-dicyclohexylene diisocyanate methane, m- and p-phenylene diisocyanate, 1,3- and 1,4-bis(isocyanate methyl) benzene, 1,5-dimethyl-

20

25

2,4-bis(isocyanate methyl) benzene, 1,3,5-trisocyanate benzene, 2,4- and 2,6-toluene diisocyanate, 2,4,6-toluene triisocyanate,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl o-, m-, and p-xylylene diisocyanate, 4,4'-diphenylene diisocyanate methane, 4,4'-diphenylene diisocyanate, 3,3'-dichloro-4,4'-diphenylene diisocyanate, naphthalene-1,5-diisocyanate, isophorone diisocyanate, and transvinylidene diisocyanate and mixtures of the aforementioned polyisocyanates.

Also, such compounds may be adducts of polyisocyanates, e.g., biurets, isocyanurates, allophanates, uretdiones, and mixtures thereof. Examples of such adducts are the adduct of two molecules of hexamethylene diisocyanate or isophorone diisocyanate and a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate and 1 molecule of water, the adduct of 1 molecule of trimethylol propane and 3 molecules of isophorone diisocyanate, the adduct of 1 molecule of pentaerythritol and 4 molecules of toluene diisocyanate, the isocyanurate of hexamethylene diisocyanate, available from Bayer under the trade designation Desmodur® N3390, the uretdione of hexamethylene diisocyanate, available from Bayer under the trade designation Desmodur® N3400, the allophanate of hexamethylene diisocyanate, available from Bayer under the trade designation Desmodur® LS 2101, and the isocyanurate of isophorone diisocyanate, available from Hüls under the trade designation Vestanate T1890. Furthermore, (co)polymers of isocyanate-functional monomers such as  $\alpha,\alpha'$ -dimethyl-m-isopropenyl benzyl isocyanate are suitable for use. Finally, the above-mentioned isocyanates and adducts thereof may be present in the form of blocked isocyanates as known to the skilled man.

Examples of compounds comprising at least two epoxy groups are solid or liquid epoxy compounds, such as the di- or polyglycidyl ethers of aliphatic,

- cycloaliphatic, or aromatic hydroxyl compounds such as ethylene glycol, glycerol, cyclohexane diol, mononuclear di- or polyvalent phenols, bisphenols such as Bisphenol-A and Bisphenol-F, and polynuclear di- or polyvalent phenols; polyglycidyl ethers of phenol formaldehyde novolac;
- 5 epoxidised divinyl benzene; epoxy compounds comprising an isocyanurate group; an epoxidised polyalkadiene such as epoxidised polybutadiene; hydantoin epoxy resins; epoxy resins obtained by epoxidising aliphatic and/or cycloaliphatic alkenes, such as dipentene dioxide, dicyclopentadiene dioxide, and vinylcyclohexene dioxide; and glycidyl
- 10 groups-comprising resins, such as polyesters or polyurethanes having two or more glycidyl groups per molecule; or mixtures of the aforementioned epoxy compounds. Preferably, use is made of the aforementioned cycloaliphatic compounds comprising two or more epoxy groups.
- 15 Alternatively, use is made of a (co)polymer of ethylenically unsaturated epoxy groups comprising compounds such as glycidyl(meth)acrylate, N-glycidyl(meth)acrylamide and/or allyl glycidyl ether and, if so desired, one or more copolymerisable, ethylenically unsaturated monomers.
- 20 Examples of compounds comprising at least two acetal groups are disclosed, int. al., in patent publications US 4,788,288, US 4,864,055, US 5,155,170, and US 5,336,807. Other suitable acetal-functional compounds include compounds obtained by reacting aminobutyraldehyde di(m)ethyl acetal (ABDA) and carboxyl ester-, isocyanate- or cyclocarbonate-
- 25 functional (co)oligomers or (co)polymers, e.g., polyester, polyacrylate, and polyurethane. An example of such a polymer includes the copolymer of glycerol cyclocarbonate methacrylate and styrene. Also, mixtures of compounds comprising at least two acetal groups can be employed.

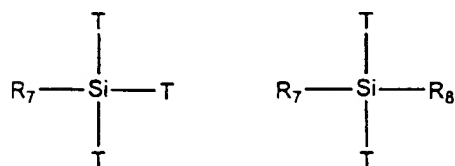
- Examples of compounds comprising at least two carboxyl groups include saturated or unsaturated aliphatic, cycloaliphatic, and aromatic polycarboxylic acids, such as malonic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, decane dicarboxylic acid, dimer fatty acid,
- 5 maleic acid, tetrahydrophthalic acid, hexahydrophthalic acid, hexahydroendomethylene tetrahydrophthalic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic acid, and mixtures thereof.
- 10 Examples of anhydride-functional compounds include radical polymers of an unsaturated cyclic anhydride monomer, e.g., maleic acid anhydride, itaconic acid anhydride, or citraconic acid anhydride. Furthermore, copolymers of said anhydride monomers and one or more ethylenically unsaturated monomers can be employed. These copolymers may contain
- 15 10-50 wt.% of anhydride groups. Examples of ethylenically unsaturated monomers are styrene, substituted styrene, vinyl chloride, vinylacetate, and esters of acrylic or methacrylic acid, e.g., methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, t-butyl(meth)acrylate, n-hexyl(meth)acrylate, 2-
- 20 ethylhexyl(meth)acrylate, cyclohexyl(meth)acrylate, 2,2,5-trimethyl cyclohexyl(meth)acrylate, and isobornyl(meth)acrylate. The anhydride-functional (co)polymer may contain small quantities, e.g., 1 to 10 wt.%, of ethylenically unsaturated carboxylic acid groups, e.g., (meth)acrylic acid. The molecular weight of the anhydride-functional (co)polymer preferably is
- 25 1000-50 000.

When the coating composition according to the present invention is used as a top coat, the aforesaid ethylenically unsaturated monomer preferably

is used in a molar ratio of 1:1 with the anhydride monomer, as described in US 4,798,745.

Alternatively, the anhydride-functional compound can be an adduct of an anhydride monomer and a functional group-comprising polymer. Examples of such adducts are: the adduct of polybutadiene or a butadiene/styrene copolymer and maleic acid anhydride; the adduct of maleic acid anhydride and a styrene/allyl alcohol copolymer esterified with an unsaturated fatty acid, resins of terpene and maleic acid anhydride; adducts of hydroxyl-comprising polymers and anhydride monomers, e.g., copolymers of hydroxyethyl(meth)acrylate or styrene/allyl alcohol and a tricarboxylic compound capable of forming anhydride groups, such as described in EP-A-0 025 917; the adduct of trimellitic acid anhydride and a polyol, such as described in EP-A-0 134 691; and the adduct of a thiol groups-comprising polymer and an unsaturated cyclic anhydride such as maleic acid anhydride, itaconic acid anhydride or citraconic acid anhydride. Also, mixtures of anhydride-functional compounds can be employed.

Examples of alkoxysilane-functional compounds are alkoxysilanes of the following general formula:



wherein T is a hydrolysable group such as -OCH<sub>3</sub>, -OC<sub>2</sub>H<sub>5</sub> or -OC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub> and

R<sub>7</sub> and R<sub>8</sub> are reactive groups selected independently from each other. Examples of such reactive groups include vinyl, aminoalkyl, epoxyalkyl,

and methacryloxyalkyl groups. Also, reaction products of alkoxy silane-functional compounds and mixtures of alkoxy silane-functional compounds and/or reaction products of these can be employed.

- 5 Examples of vinyl-functional alkoxy silanes include vinyl triethoxy silane and vinyl trimethoxy silane. As an example of a reaction product of a vinyl-functional alkoxy silane may be mentioned the silicone resin formed by the reaction of  $(\text{CH}_2=\text{CHSiO}_{3/2})_x(\text{R}_2\text{SiO})_y$  and styrene.
- 10 Reaction products of amino-functional alkoxy silanes can be made by reacting such silanes with inorganic acids HA:  

$$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{T})_3 + \text{HA} \rightarrow \text{A-NH}(\text{CH}_2)_3\text{Si}(\text{T})_3$$

wherein A is the acid radical ion, or with esters of organic acids  $\text{R}_9(\text{COOR}_{10})_n$ , wherein n is an integer of at least 1,  $\text{R}_9$  is a linear or

15 branched, optionally unsaturated, alkane radical, and  $\text{R}_{10}$  is a lower alkyl group, e.g., a  $\text{C}_{1-4}$  alkyl group, e.g.:

$$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{T})_3 + \text{R}_9\text{COOR}_{10} \rightarrow \text{R}_9\text{CO-NH}(\text{CH}_2)_3\text{Si}(\text{T})_3$$

$$2 \text{NH}_2(\text{CH}_2)_3\text{Si}(\text{T})_3 + 1 \text{R}_{10}\text{OOCR}_9\text{COOR}_{10} \rightarrow$$

$$(\text{T})_3\text{Si}(\text{CH}_2)_3\text{NH-OCR}_9\text{CO-NH}(\text{CH}_2)_3\text{Si}(\text{T})_3.$$
- 20 For example, the adduct of 1 mole diethyl malonate and 2 moles of 3-amino propyl trimethoxy silane is a suitable alkoxy silane containing compound. Also suitable for use are reaction products of amino-functional alkoxy silanes and isocyanate-functional compounds.
- 25 One example of a reaction product of an epoxy-functional silane compound is the reaction product of  $\beta$ -(3,4-epoxycyclohexyl) ethyl trimethoxy silane and amines, acids, and alcohols.

Examples of reaction products of methacryloxyalkyl trialkoxysilane are reaction products of  $\gamma$ -methacryloxypropyl trimethoxysilane and  $\gamma$ -methacryloxypropyl tri( $\beta$ -methoxyethoxy)silane and vinyl-functional monomers, such as styrene and methyl methacrylate.

5

Examples of suitable amino resins are urea resins, guanamine resins, and melamine resins, and mixtures of these. Examples of urea resins are etherified methylol urea, butyl urea, and isobutyl urea. One example of a guanamine resin is tetra(methoxymethyl)benzoguanamine. Examples of  
10 melamine resins are hexa(methoxymethyl)melamine (HMMM) and isobutylated melamine.

15

In addition to the disclosed BOE- and SOE-functional compounds and said hydroxyl-reactive compounds other compounds may be present in the coating composition according to the present invention. Such compounds may be main binders and/or reactive diluents comprising reactive groups which may be cross-linked with the aforesaid hydroxyl-functional compounds and/or hydroxyl-reactive compounds. Examples include hydroxyl-functional binders, e.g., polyester polyols such as described in H.  
20 Wagner et al., Lackkunstharze, 5th ed., 1971 (Carl Hanser Verlag, Munich), polyether polyols, polyacrylate polyols, polyurethane polyols, cellulose acetobutyrate, hydroxyl-functional epoxy resins, alkyds, and dendrimeric polyols such as described in WO 93/17060. Also, hydroxyl-functional oligomers and monomers, such as castor oil and trimethylolpropane may  
25 be present. Finally, ketone resins, aspartyl acid esters, and latent or non-latent amino-functional compounds such as oxazolidines, ketimines, aldimines, diimines, secondary amines, and polyamines may be present. These and other compounds are known to the skilled person and are mentioned, int. al., in US 5,214,086.



The ratio of hydroxyl-reactive groups to hydroxyl groups ranges from 50 to 300 eq.%, preferably from 70 to 250 eq.%

- 5 The invention further encompasses a process for curing the present coating composition. More particularly, the latent hydroxyl groups of the BOE or SOE-functional compound have to be deblocked and reacted with the hydroxyl-reactive groups of the second compound to allow the present coating composition to be cured.
- 10 The deblocking of the latent hydroxyl groups of the BOE and SOE compounds takes place under the influence of water in the form of, e.g., moisture from the air or added water. This deblocking is preferably catalysed by a first catalyst selected from the group of Lewis acids, such as
- 15  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$  and  $\text{ZrCl}_4$  and organic complexes thereof, e.g.,  $\text{BF}_3\text{Et}_2\text{O}$ ,  $\text{BF}_3\text{-2CH}_3\text{COOH}$ ,  $\text{BF}_3\text{-2H}_2\text{O}$ ,  $\text{BF}_3\text{-H}_3\text{PO}_4$ ,  $\text{BF}_3\text{-(CH}_3)_2\text{O}$ ,  $\text{BF}_3\text{-THF}$ ,  $\text{BF}_3\text{-2CH}_3\text{OH}$ ,  $\text{BF}_3\text{-2C}_2\text{H}_5\text{OH}$ , and  $\text{BF}_3\text{-C}_6\text{H}_5\text{CH}_2$ , and Brønsted acids. Preferably, use is made of Brønsted acids having a  $\text{pK}_a < 3$ , such as a mono- or dialkyl phosphate, a carboxylic acid
- 20 having at least one chlorine and/or fluorine atom, an alkyl or aryl sulphonic acid or an (alkyl)phosphoric acid, more particularly methane sulphonic acid, paratoluene sulphonic acid, optionally substituted naphthalene sulphonic acids, dodecyl benzene sulphonic acid, dibutyl phosphate, trichloroacetic acid, phosphoric acid, and mixtures thereof.
- 25 Said first catalysts may be blocked, if so desired, resulting in the release of the Lewis or Brønsted acid under the influence of, e.g., electromagnetic irradiation (light or UV), heat or moisture. Acid generating photoinitiators are described, *int. al.*, in G. Li Bassi et al., "Photoinitiators for the

Simultaneous Generation of Free Radicals and Acid Hardening Catalysts,"  
Radcure '86 Proceedings, e.g. 2-methyl-1-[4-(methylthio)phenyl]-2-[4-  
methylphenylsulphonyl] propan-1-one (MDTA), ex. Fratelli Lamberti Spa,  
Varese, Italy. Alternatively, use may be made of Lewis acid generating  
5 compounds such as Irgacure® 261 ex Ciba Geigy and trimethyl silyl  
benzene sulphonic ester.

The first catalyst can be used alone or as a mixture of catalysts in effective  
amounts. The term effective amount in this case is dependent on the use of  
10 the BOE- or SOE-functional compound. When the BOE- or SOE-functional  
compound is used as a main binder, sufficient catalyst will have to be  
present to hydrolyse practically all BOE- or SOE-functional compounds.  
However, if the BOE- or SOE-functional compound is used primarily as a  
reactive diluent while other compounds are present as main binders, the  
15 hydrolysis of at least a portion of the BOE- or SOE-functional compound  
will suffice.

Amounts of 0 to 10 wt.% relative to the BOE- and SOE-functional  
compounds of the first catalyst may be sufficient. Preferably, 0,3 to 8 wt.%,  
20 more specifically, 0,5 to 6 wt.%, will be present.

The reaction of the deblocked hydroxyl groups of the BOE or SOE  
compound, the hydroxyl-reactive groups of the second compound, and,  
optionally, third compounds present in the composition comprising hydroxyl  
25 groups or hydroxyl-reactive groups, takes preferably place under the  
influence of a second catalyst. Such catalysts are known to the skilled  
person. The second catalyst is used in an amount of 0 to 10 wt.%,  
preferably 0,001 to 5 wt.%, more preferably in an amount of 0,01 to 1 wt.%,  
calculated on solid matter (i.e., the amount of BOE or SOE, the hydroxyl-

reactive compound, and, optionally, the above-mentioned third compounds).

As an example for the various hydroxyl-reactive groups the following  
5 catalysts may be mentioned. Polyisocyanates: dimethyl tin dilaurate, dibutyl tin dilaurate, dibutyl tin diacetate, tin octoate, zinc octoate, aluminum chelate, and dimethyl tin dichloride; polyepoxy compounds: tertiary amines and Lewis acids such as  $\text{BF}_3$  or organic complexes thereof; polyacetal compounds: paratoluene sulphonic acid and dodecyl benzene sulphonic  
10 acid; polycarboxylic compounds: dodecyl benzene sulphonic acid, polyanhydride compounds: organotin compounds; alkoxysilane compounds: organotin compounds, phosphoric acid, paratoluene sulphonic acid, dodecyl benzene sulphonic acid, and tertiary amines; and amino resins: dodecyl benzene sulphonic acid.

15

As can be noted from the above, the first and the second catalyst may be the same in some coating compositions. In that case, the amount of catalyst may be higher than indicated for the first or second catalyst alone.

20 The coating composition according to the invention may be part of a components system, for instance a 2-component system. For example, one component may comprise both the BOE- or SOE-functional compound and the hydroxyl-reactive compound. The second component may comprise the catalyst for the hydrolysis of the BOE- or SOE-functional compound

25

Alternatively, a 3-component system may be employed. For example, one component may comprise the BOE- or SOE-functional compound. A second component may comprise the hydroxyl-reactive component. A third

component may comprise the catalyst for the hydrolysis of the BOE- or SOE-functional compound.

- In addition, a coating composition such as described may contain the usual
- 5 additives such as solvents, pigments, fillers, leveling agents, emulsifiers, anti-foaming agents and rheology control agents, reducing agents, antioxidants, HALS-stabilisers, UV-stabilisers, water traps such as molecular sieves, and antisetling agents.
- 10 Application onto a substrate can be via any method known to the skilled person, e.g., via rolling, spraying, brushing, flow coating, dipping, and roller coating. Preferably, a coating composition such as described is applied by spraying.
- 15 The coating composition of the present invention may be applied to any substrate. The substrate may be, for example, metal, e.g., iron, steel, and aluminum, plastic, wood, glass, synthetic material, paper, leather, or another coating layer. The other coating layer may be comprised of the coating composition of the current invention or it may be a different coating
- 20 composition. The coating compositions of the current invention show particular utility as clearcoats (over base coats, water-borne and solvent-borne), base coats, pigmented topcoats, primers, and fillers. The compositions are particularly suitable for refinishing motor vehicles and transportation vehicles and in finishing large transportation vehicles such
- 25 as trains, trucks, buses, and aeroplanes.

The applied coating composition can be cured very effectively at a temperature of, e.g., 0-50°C. If so desired, the coating composition may be baked, e.g., at a temperature in the range of 50-120°C.

The present BOE-functional compound can be prepared in several ways.

One such way is the transesterification of a polyol in an appropriate solvent. Examples of such polyols include glycerol, trimethylol propane, and pentaerythritol. The transesterification agent can be a trialkyl orthoester selected from the group of triethyl orthoformate, triethyl orthoacetate, and triethyl orthopropionate. Preferably, use is made of solvents which are inert to the transesterification reaction, e.g., diethylene glycol dimethyl ether and tetraethylene glycol dimethyl ether. The catalyst for such a reaction may be a strong acid, e.g., paratoluene sulphonic acid or  $\text{BF}_3\text{Et}_2\text{O}$ . Such a process is described in T. Endo et al., Polymer Journal, Vol. 13 (1981), p. 715.

When the polyol selected is pentaerythritol, a BOE group comprising a hydroxyl group is formed. This BOE group is converted into a BOE-functional compound by means of a transesterification reaction or by reaction with an acid chloride. In this way a hydroxyl-functional BOE group can be linked via transesterification to a saturated or unsaturated carboxylic acid, preferably one having not more than 20 carbon atoms. The resulting BOE-functional compound has the advantage of being non-volatile or hardly volatile because of the high molecular weight, while, surprisingly, the viscosity remains low. For this reason the BOE-functional compound is highly suited to be used as a reactive diluent. When the carboxylic acid group is unsaturated, the present coating composition comprising such a BOE-functional compound can be cured in two ways, i.e., via the hydrolysed BOE group as described above and via the unsaturated compound.

Also, the aforesaid hydroxyl-functional BOE group can be provided with a vinyl group via a transesterification reaction with a (meth)acrylate. By polymerisation under the influence of radicals using a vinyl-comprising BOE a BOE-functional polyacrylate can be prepared.

5

A BOE-functional polyacrylate can further be prepared by the transesterification of a polyacrylate with a hydroxyl-functional BOE group. In this case it is preferred to employ a polyacrylate having short-chain esters, preferably esters having 1-4 carbon atoms. The advantage of such  
10 a polyacrylate is that after the transesterification reaction the resulting alcohol groups can be isolated, e.g., by distillation. In general, every polymer having an ester group as side group can be provided with BOE groups via said transesterification. As examples of polymers may be mentioned polyesters, polyethers, polyamides, and polyurethanes.

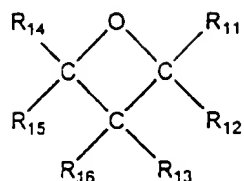
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Alternatively, the hydroxyl-functional BOE group can be provided with groups which are reactive or not using, e.g., isocyanate-functional compounds. Furthermore, two or more BOE-functional groups can be interlinked using a di- or polyisocyanate-functional compound. In this way  
20 also the hydroxyl-functional BOE group can be linked to, e.g., hydroxyl-functional polymers, e.g., polyester polyols, polyether polyols, and polyacrylate polyols.

Also, BOE-functional compounds can be prepared by converting the  
25 corresponding ester-functional oxetane compounds with  $\text{BF}_3\text{Et}_2\text{O}$ , as described by E.J. Corey et al., Tetrahedron Letters, 24 (1983), pp. 5571-5574.

Oxetane compounds have the following structure:

30



wherein  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ ,  $R_{14}$ , and  $R_{15}$  are independently from each other selected from the group of hydrogen and a linear or branched alkyl group having 1-10 carbon atoms; and  
 $R_{16}$  is a linear or branched alkyl group having 1-4 carbon atoms substituted with a nucleophilic group selected from the group of hydroxyl, mercaptan, and a primary or secondary amine, and/or with an electrophilic group selected from halogen and derivatives of methane sulphonate, p-toluene sulphonate, and trifluoromethane sulphonate.

Preferably,  $R_{16}$  is hydroxymethyl, hydroxyethyl, chloromethyl or chloroethyl. The preparation of oxetane compounds comprising a hydroxyl group is described in J.B. Pattison, J. Am. Chem. Soc., 79 (1957), pp. 3455-3456.  
 Said hydroxyl-functional oxetane compounds can be converted into ester group-comprising oxetanes via a transesterification reaction with suitable esters  $R_{17}(\text{COOR}_{18})_n$ , wherein  $n$  is an integer of at least 1,  $R_{17}$  is a saturated or unsaturated alkyl, aryl, or acyl radical having 1-40 carbon atoms, optionally substituted with a reactive group such as vinyl, carbonyl, carboxyl ester, or hydroxyl, and  $R_{18}$  is an alkyl group having 1-4 carbon atoms.  $R_{18}$  preferably is methyl, ethyl, or propyl. The alcohols  $R_{18}\text{OH}$  released on transesterification are isolated from the reaction mixture, e.g., by means of distillation. Such suitable esters may be, for example, the methyl ester of a fatty acid and mixtures of fatty acid, e.g. Edenor ME C6-

10, ex. Henkel, and the dimethyl ester of a dimer fatty acid, e.g. Pripol 1009, ex. Unichema.

Also, ester group-comprising oxetane compounds can be polymers, with  
5 the oxetane compounds being terminal groups or side groups. In that case,  $R_{17}$  can be a polymeric group such as polyester, polyether, polyacrylate, polyamide or polyurethane. Suitable polyesters can be obtained by the nucleophilic addition of carbanions to  $\alpha,\beta$ -unsaturated carbonyl compounds. Likewise suitable are ester group terminated polyesters  
10 derived from polycarboxylic acids, polyols, or ester-forming equivalents thereof. Preferably, the aforesaid  $R_{18}$  groups are employed.

Other examples include the adduct of the conversion of diethyl fumarate and diethyl malonate to tetraethyl ester of 1,1,2,3-propane tetracarboxylic  
15 acid and a hydroxyl-functional oxetane. In the presence of a diol or polyol a terminal oxetane-functional polyester is formed.

The hydroxyl-functional oxetane compounds also can be converted with the aid of acid chlorides  $R_{17}(\text{COCl})_n$ .

20 Preferably,  $R_{17}$  is a group having a high molecular weight, such as pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or the aforesaid polymers. The resulting BOE compound is non-volatile or hardly volatile because of the high molecular weight, and on account of its surprisingly low viscosity is  
25 pre-eminently suited to be used as a reactive diluent.

Halogen-functional oxetanes can be converted into ester-functional oxetanes by reacting them with carboxylate salts of, e.g., silver or with



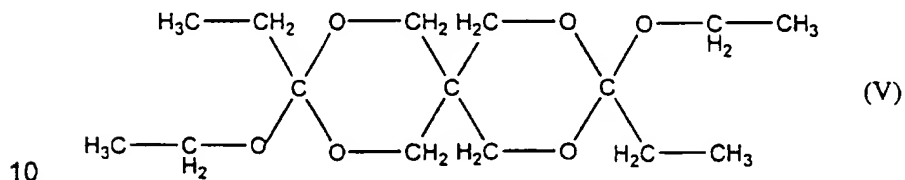
ammonium compounds such as substituted or unsubstituted ammonium salts.

It has now been found that the conversion of the ester-functional oxetane compound in a BOE-functional compound already takes place in the presence of a catalytic amount of a strong Brønsted or Lewis acid or organic complexes thereof. Lewis acids are preferred. Examples of Lewis acids are:  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$ , and  $\text{ZrCl}_4$  and organic complexes thereof, e.g.,  $\text{BF}_3\text{Et}_2\text{O}$ ,  $\text{BF}_3\cdot 2\text{CH}_3\text{COOH}$ ,  $\text{BF}_3\cdot 2\text{H}_2\text{O}$ ,  $\text{BF}_3\cdot \text{H}_3\text{PO}_4$ ,  $\text{BF}_3\cdot (\text{CH}_3)_2\text{O}$ ,  $\text{BF}_3\cdot \text{THF}$ ,  $\text{BF}_3\cdot 2\text{CH}_3\text{OH}$ ,  $\text{BF}_3\cdot 2\text{C}_2\text{H}_5\text{OH}$ , and  $\text{BF}_3\cdot \text{C}_6\text{H}_5\text{CH}_2$ . More preferred are  $\text{BF}_3\text{Et}_2\text{O}$ ,  $\text{BF}_3\cdot 2\text{CH}_3\text{COOH}$ , and  $\text{SnCl}_4$ . Amounts of 0,001-0,1 mole of catalyst per mole of oxetane compound are preferred, more preferably 0,004-0,08 mole/mole. It has further been found that the conversion already takes place in the presence of a small amount of solvent, and even without solvent if so desired. The term solvent in this connection refers to those solvents which are conventionally employed in the field of organic chemistry and have been described for the conversion of oxetane compounds. The conversion takes place in the range of -100 to 200°C, preferably in the range of 0 to 80°C. The conversion time is in the range of 30 minutes to 2 days and can result in a yield of more than 90%.

Various methods can be employed to prepare SOE-functional compounds. One such method of preparation is the reaction of an epoxy-functional compound such as butyl glycidyl ether with a lactone such as caprolactone or butyrolactone. Alternatively, SOE-functional polymers can be prepared from epoxy-functional polymers, e.g., polyacrylates of glycidyl(meth)acrylate, using lactones, or from polylactones using

monoepoxides. Again, use may be made of catalysts such as Lewis or Brønsted acids, preferably paratoluene sulphonic acid or  $\text{BF}_3\text{Et}_2\text{O}$ .

Further, a SOE-functional compound can be prepared by reacting  
 5 pentaerythritol and triethyl orthopropionate in the presence of paratoluene sulphonic acid with a specific trimethyl benzene being used as solvent. Surprisingly, in this way very selectively a compound having two SOE groups of the following structure



was synthesised.

The invention will be elucidated further with reference to the following  
 15 examples.

### Examples

In the examples the following abbreviations are used:

- |    |                                |                                    |
|----|--------------------------------|------------------------------------|
|    | paratoluene sulphonic acid     | : PTSA                             |
| 5  | dibutyl tin dilaurate          | : DBTL                             |
|    | methyl amyl ketone             | : MAK                              |
|    | ethyl amyl ketone              | : EAK                              |
|    | boron trifluoride etherate     | : $\text{BF}_3\text{Et}_2\text{O}$ |
|    | dibutyl phosphate              | : DBP                              |
| 10 | dodecyl benzene sulphonic acid | : DDBSA                            |

In the examples the following compounds are used.

- Edenor® ME C6-10, ex. Henkel, a mixture of methyl ester of fatty acids,  
15 with the following chain length distribution: C6 1-8%, C8: 40-60%, C10: 30-50%, C12: 0-5%.

Byk 333 is a silicone surface additive, ex. Byk Chemie.

Byk 300 is a flow additive, ex. Byk Chemie.

- 20 Byk 322 is a flow additive, ex. Byk Chemie.

Byk 355 is a flow additive, ex. Byk Chemie.

Disperbyk 110 is a dispersing agent, ex. Byk Chemie.

Disperbyk 166 is a dispersing agent, ex. Byk Chemie.

- 25 Nacure 5076 is 70% DDBSA in isopropanol, ex. King Industries

Fascat 4202 is a 10% DBTL solution in xylene, ex. Air Products.

Desmodur® N3400 is an aliphatic polyisocyanate based on the uretdione of hexamethylene diisocyanate, ex. Bayer.

Desmodur® VL50 is an aromatic polyisocyanate based on diphenylmethane diisocyanate, ex. Bayer.

Desmodur® N3390 is an aliphatic polyisocyanate based on the isocyanurate of hexamethylene diisocyanate, ex. Bayer.

- 5 Desmodur® L75 is an aromatic polyisocyanate based on toluene diisocyanate, ex. Bayer.

Desmodur® LS2025 is an aliphatic low viscous polyisocyanate based on hexamethylene diisocyanate, ex. Bayer.

- 10 Vestanat® T1890E is a cycloaliphatic polyisocyanate based on the isocyanurate of isophorone diisocyanate, ex. Hüls.

Hardener MS, ex. Sikkens, comprises Desmodur® N3390 (S.C.=36%).

- 15 The polyester polyol A is a high solids polyester having a hydroxyl number of 148, an acid number of 8,8, and an Mn of 1888 (GPC, polystyrene standard). The polyester had a viscosity of 7 Pa.s in an 81%-solution in butyl acetate.

- 20 The polyester polyol B is based upon 1,4-dimethanol cyclohexane, hexahydrophthalic anhydride, 3,5,5-trimethyl hexanoic acid, trimethylol propane and glycidyl ester of a 1,1-disubstituted branched decane monocarboxylic acid. The polyester polyol has a solids content of 70%, a viscosity of 580 mPa.s at 20 °C, a Tg of -3°C, an acid value of 0.2, a hydroxyl number of 160, a Mn of 1090 and a Mw of 3140 (as measured by gel permeation chromatography using polystyrene as a standard).

- 25 The polyester polyol C is based upon phthalic anhydride, hexahydrophthalic anhydride, 3,5,5-trimethyl hexanoic acid, and trimethylol propane. The polyester polyol has a solids content of 80,5 %, a viscosity of 7,5 Pa.s at 20 °C, a Tg of -2°C, an acid value of 9,3, a hydroxyl number of

145, a Mn of 1900 and a Mw of 4500 (as measured by gel permeation chromatography using polystyrene as a standard).

Autoclear MS 2000, ex. Sikkens, comprises a polyacrylate polyol resin and 0,02% DBTL (on solids). The S.C. is 46%.

- 5 Resimene RF 4518 is a melamine resin, ex. Monsanto.

Irgazin DPP Red BO is a bright red pigment, ex. Ciba-Geigy.

Zinc phosphate ZP10 is an anti-corrosive pigment, ex. Heubach.

Tioxide TR92 is an titanium dioxide pigment, ex. Tioxide.

10

Aerosil R972 is a silica compound, ex. Degussa.

China clay grade C is an extender, ex. ECC International Ltd.

Blank fix N is an extender, ex. Sachtleben Chemie GmbH.

15

Tinuvin 1130 is a UV stabilizer, ex. Ciba-Geigy.

Tinuvin 123 is a HALS stabilizer, ex. Ciba-Geigy.

Solvesso 100 is a blend of aromatic solvents, ex. Exxon.

- 20 1.2.3. Thinner slow, ex. Sikkens, is a mixture of solvents.

Unless otherwise stated, the properties of the coating compositions and the resulting films are measured as follows.

- 25 The viscosity was measured in a DIN flow cup number 4 according to DIN 53211-1987. The viscosity is reported in seconds.

The potlife is defined as the time period wherein the viscosity of the coating composition after initial mixing of all compounds is doubled.

The drying time is measured as follows. The coating composition is applied with a draw bar or by spraying onto steel plate. Using a BK Drying Recorder® the time until the end of the third phase of the layer's drying is measured. The term third phase refers to the drying phase during which the BK Drying Recorder®'s needle makes a small, tight scratch in the film which no longer fills up.

A coating is "touch dry" when the mark formed by firm pushing with the thumb disappears after 1 or 2 minutes.

The solids content (S.C.) is measured after 1 day drying at room temperature followed by 1 hour at 150°C. The theoretical maximum S.C. is the S.C. at which all BOE or SOE is assumed to be hydrolysed and bound in the dry film. The theoretical minimum S.C. is the S.C. at which it is assumed that all BOE or SOE has evaporated from the dry film.

Gloss is measured according to ISO 2813:1994. The gloss is expressed in Gloss units.

Solvent resistance is measured by exposing coated steel panels to MEK. The time required to soften the paint film to a pencil hardness of 2b gives the resistance.

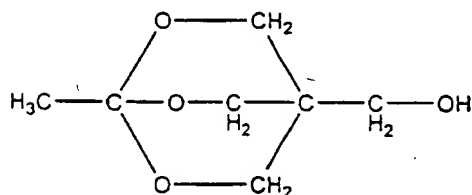
#### Example 1

##### Preparation of 4-methylol-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE 1)

Into a flask equipped with a stirrer, a distilling column, a nitrogen inlet, a heating jacket, and a thermometer were charged 486 g of triethyl orthoacetate, 408 g of pentaerythritol, 300 g of diethylene glycol dimethyl

ether, and 0,9 g of PTSA. The mixture was gradually heated to 170°C over a period of 5 hours. During this time 490 g of distillate were obtained. The distillate contained mostly ethanol and small amounts of diethylene glycol dimethyl ether. The temperature was lowered to 100°C, and the remaining diethylene glycol dimethyl ether was distilled off under reduced pressure (30 mbar). The residue was subjected to vacuum distillation. The fraction having a boiling temperature of 126-130°C at a pressure of 4 mbar yielded 426 g of oil. This oil solidified to a clear solid having a melting point of 99°C and had the following structure

10



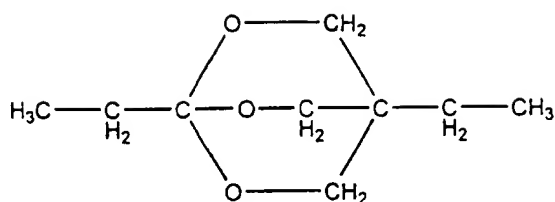
### Example 2

#### 15 Preparation of 1,4-diethyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE 2)

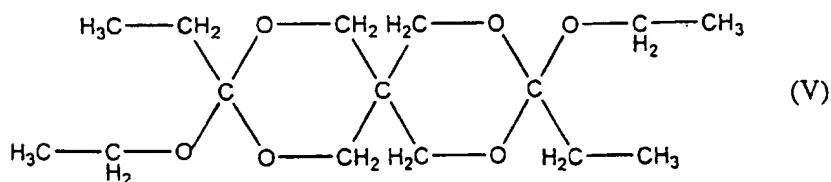
Into a flask as specified in Example 1 were charged 529 g of triethyl orthopropionate, 402 g of trimethylol propane, 330 g of diethylene glycol dimethyl ether, and 0,9 g of PTSA. The mixture was heated for 0,5 hour at 140°C, with 402 g of ethanol being distilled off. The temperature was lowered to 100°C, and the remaining diethylene glycol dimethyl ether was distilled off under reduced pressure. The residue was subjected to vacuum distillation. The fraction having a boiling temperature of 54°C at a pressure of 0,5 mbar yielded 370 g of clear, low-viscous liquid having a boiling point of 223°C at atmospheric pressure and with the following structure

25

30

Example 3Preparation of a spiro-orthoester (SOE 1)

- 5 Into a flask as specified in Example 1 were charged 125 g of trimethyl benzene, 89 g of triethyl orthopropionate, 68 g of pentaerythritol, and 0,125 g of PTSA. The mixture was heated for 4 hours at 140°C. After just 2 hours the ethanol distillation came to a halt. In all, only 36 g of ethanol were distilled off. Only a portion of the pentaerythritol dissolved in the reaction
- 10 mixture. After cooling the mixture was neutralised with potassium carbonate, and all solids were filtered off. Trimethyl benzene and traces of unreacted triethyl orthopropionate were distilled off under reduced pressure, and the residue was subjected to vacuum distillation. The fraction having a boiling temperature of 140-145°C at a pressure of 1 mbar yielded
- 15 37 g of oil. After analysis via  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy it was found that a spiro-orthoester compound of the following structure had formed



20

Example 4Preparation of a spiro-orthoester (SOE 2)

Into a flask equipped with a stirrer, a reflux condenser, a dropping funnel, a heating jacket, and a thermometer were charged 43 g of  $\gamma$ -butyrolactone,

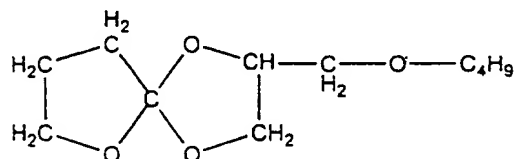


65 g of diethyl ether, and 1,4 g of a 35%-solution of  $\text{BF}_3\text{Et}_2\text{O}$  in diethyl ether. To this mixture were added in the course of 1 hour 93 g of butyl glycidyl ether. The reaction was slightly exothermic. By means of external cooling the temperature was maintained in the range of 23-28°C. After the

5 addition of the butyl glycidyl ether the mixture was kept at said temperature for 3 hours with continuous stirring. Next, the reaction mixture was heated to reflux for one hour. After cooling to room temperature, 2 g of sodium carbonate were added and stirring was continued overnight at room temperature. The solids were filtered off, and 1 more g of sodium carbonate

10 was added. Diethylether was distilled off at reduced pressure at room temperature. The residue was subjected to vacuum distillation. The fraction having a boiling point in the range of 45-65°C at a pressure of 0,1 mbar yielded 31 g of clear liquid. After analysis ( $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy) it was found that a spiro-orthoester of the following structure had formed

15



### Example 5

#### A: Preparation of 3-ethyl-3-hydroxymethyl oxetane

20 This oxetane was prepared as described by J.B. Pattison, J. Am. Chem. Soc., 79 (1957), p. 3455 and J.V. Crivello et al., J.M.S. - Pure Appl. Chem., A30 (1993), p. 189.

Trimethylol propane (1023,6 g, 7,63 moles), diethyl carbonate (901,3 g, 7,63 moles), and potassium hydroxide (0,77 g) were weighed into a 5-l three-neck flask. The reaction mixture was heated to reflux temperature

25 (123°C). After the reaction temperature had been lowered to 105°C, the

distilling off of ethanol was started. The reaction temperature was increased to 150°C. On conclusion of the distillation vacuum (15 mbar) was used to remove the remaining ethanol and diethyl carbonate from the reaction mixture. Next, the reaction mixture was heated to 220°C. Gas formation was observed, and under reduced pressure (40 mbar) at 130°C a clear oil came over which was identified as 3-ethyl-3-hydroxymethyl oxetane. The yield was 698,0 g (79%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0,9 (t,  $^3\text{H}$ ); 1,7 (q,  $^2\text{H}$ ); 3,1 (t,  $^1\text{H}$ ); 3,7 (d,  $^2\text{H}$ ); 4,4 (dd,  $^4\text{H}$ ).

10 B: Preparation of 3-ethyloxetan-3-yl methyl laurate

Into a three-neck flask (1 l) equipped with a Vigreux distillation column were weighed ethyl laurate (228,4 g, 1,0 moles), 3-ethyl-3-hydroxymethyl oxetane (116,0 g, 1,0 mole), dibutyl tin oxide (0,34 g), and xylene (25,0 g). The reaction mixture was heated to reflux temperature. At 170°C ethanol began to distill off. The reaction mixture was heated such that the ethanol distillation proceeded smoothly. At a reaction temperature of 250°C all ethanol had distilled off. The xylene was removed under reduced pressure. According to  $^1\text{H}$  NMR analysis, the residue (298,7 g) was pure 3-ethyloxetan-3-yl methyl laurate. The product solidified at room temperature.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0,9 (2 x t,  $^6\text{H}$ ); 1,3 (br s,  $^{16}\text{H}$ ); 1,65 (m,  $^2\text{H}$ ); 1,8 (q,  $^2\text{H}$ ); 2,4 (t,  $^2\text{H}$ ); 4,2 (s,  $^2\text{H}$ ); 4,45 (dd,  $^4\text{H}$ ).

C: Preparation of 4-ethyl-1-undecyl-2,6,7-trioxabicyclo[2.2.2]octane

This reaction was carried out under a nitrogen atmosphere. 3-ethyloxetan-3-yl methyl laurate prepared as specified in Example 5B (270,0 g, 904  $\mu\text{moles}$ ) and  $\text{BF}_3\text{Et}_2\text{O}$  (1,0 g) were mixed in an Erlenmeyer flask. The reaction mixture was hazy but became clear after some time. After it had been left to stand overnight  $^1\text{H}$  NMR analysis showed that virtually all oxetane ester had been converted into the corresponding BOE compound.

The reaction mixture was subjected to a vacuum distillation. At 155°C/1 mbar 4-ethyl-1-undecyl-2,6,7-trioxabicyclo[2.2.2]octane came over. The yield was 205 g (76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0,75 (t, <sup>3</sup>H); 0,8 (t, <sup>3</sup>H); 1,2 (br s, <sup>16</sup>H); 1,35 (br m, <sup>2</sup>H); 1,50 (t, <sup>2</sup>H); 3,80 (s, <sup>6</sup>H).

5

#### Example 6

##### A: Preparation of 3-ethyl-3-hydroxymethyl oxetane

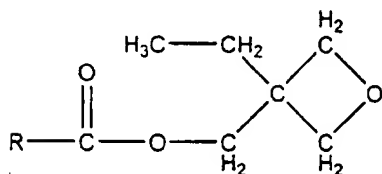
Trimethylol propane (1489 g, 11,1 moles), dimethyl carbonate (1201 g, 13,3 moles), and potassium hydroxide (5,38 g) were weighed into a 5-l  
10 three-neck flask equipped with a stirrer, a reflux condenser, a nitrogen inlet, a heating jacket, and a thermometer. The reaction mixture was heated to reflux temperature (86°C) and kept at reflux for 2 hours. The temperature lowered to 80°C. Subsequently, the temperature of the reaction mixture was increased to 155°C in 6 hours. On conclusion of the distillation 890 g  
15 distillate were obtained containing mostly methanol and dimethyl carbonate in a ratio of 60 to 40. The temperature was lowered to 120°C and under vacuum (200-40 mbar) the remaining ethanol and dimethyl carbonate was removed from the reaction mixture (about 14 g). Next, the reaction mixture was gradual heated to 180°C. Under a stream of CO<sub>2</sub> and reduced  
20 pressure (60-40 mbar) a clear oil came over which was identified as 3-ethyl-3-hydroxymethyl oxetane. The yield was 860 g.

##### B: Preparation of 3-ethyloxetan-3-yl methyl ester of fatty acids

Into a flask (5 l) equipped as in Example 6A were weighed Edenor® ME  
25 C6-10 (1268 g, 7,4 moles), 3-ethyl-3-hydroxymethyl oxetane of example 6A (858,4 g, 7,4 moles), and dibutyl tin oxide (2,13 g). The reaction mixture was heated to reflux temperature. At 150°C methanol began to distill off. The reaction mixture was heated in 5 hours to 240°C. 197 g distillate were obtained comprising mainly methanol (83% of theory). The temperature

was reduced to 150°C and under vacuum (40 mbar) about 40 g of remaining distillate was removed. It was found that the residue (1834 g) had the following structure, wherein R is a mixture of pentyl, heptyl, nonyl, and undecyl groups:

5

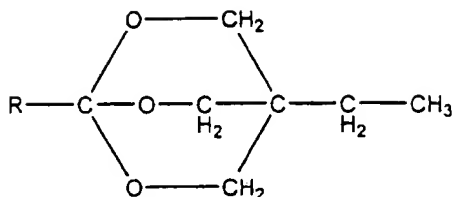


C: Preparation of crude 4-ethyl-1-(C5-11 alkyl)-2,6,7-trioxabicyclo[2.2.2]octane (BOE 3A)

- 10 This reaction was carried out under a nitrogen atmosphere. 3-ethyloxetan-3-yl methyl ester of fatty acids prepared as specified in Example 6B (1834 g) was cooled to 50°C and  $\text{BF}_3 \cdot 2\text{CH}_3\text{COOH}$  (4.59 g) was carefully added thereto. The reaction mixture was heated to 70°C and kept at that temperature for 6 hours. Next, the reaction mixture was cooled to 50°C and
- 15 2.45 g triethyl amine was added to neutralize the catalyst. To the resulting residue 1% of a filter additive was added and filtrated. The filtrate was 1730 g and contained about 78% BOE and 22% polymer.

D: Preparation of pure 4-ethyl-1-(C5-11 alkyl)-2,6,7-trioxabicyclo[2.2.2]octane (BOE 3B)

- 20 Into a flask (5 l) equipped as in Example 6A were weighed 1730 g of crude BOE 3A prepared in Example 6C. The reaction mixture was heated to 140°C and a reduced pressure of 40 mbar. The temperature was increased gradually to 240°C whereby a clear liquid came over. 1235 g was collected
- 25 of what was found to be pure BOE 3B of the following formula, wherein R is a mixture of C5, C7, C9, and C11 alkyl groups:



5

Example 7A: Preparation of dimethyl ester of dimer fatty acid

- Pripol 1009 dimer fatty acid, ex. Unichema (742 g, 1,31 moles, 2,62 eq. acid), methanol (2000 g), and Amberlyst 15 acidic ion exchange resin from
- 10 Rohm & Haas (40 g) were weighed into a flask equipped with a stirrer, a reflux condenser, a nitrogen inlet, a thermocouple, and a heating jacket. The reaction mixture was heated to reflux temperature (65°C). At intervals samples were analyzed by infrared spectroscopy. Heating was continued until the carbonyl signal of the carboxylic acid at 1710 cm<sup>-1</sup> disappeared in
- 15 the infrared spectrum (about 18 hrs.). The reaction mixture was cooled to room temperature and the liquid decanted from the ion exchange resin. The liquid was subjected to rotary evaporation to evaporate substantially all methanol. The evaporation residue was diluted with diethylether (300 g). The ether solution was washed with, aqueous 10% sodium carbonate
- 20 solution (500 g) and subsequently with water (500 g) in three portions. Magnesium sulfate (30 g) was added to the organic layer and stirred for 12 hrs. The liquid was filtered and the diethylether distilled off by rotary evaporation. The evaporation residue was the dimethyl ester of Pripol 1009 as a colourless oil (752 g, 96% of theory).

25

B: Preparation of di-3-ethyloxetan-3-yl methyl ester of dimer fatty acid

Into a flask equipped with a stirrer, a distillation head, a nitrogen inlet, a thermocouple, a vacuum line, and a heating jacket were weighed the dimethyl ester of Pripol 1009 of Example 7A (713,5 g, 2,4 eq.), 3-ethyl-3-  
5 hydroxymethyl oxetane of Example 6A (278,4 g, 2,4 moles), and dibutyl tin oxide (1,0 g). The reaction mixture was gradually heated in 4 hours to 240°C. During this time 47 g methanol were distilled off. The temperature was reduced to 160°C and vacuum was applied. The pressure was gradually decreased to 20 mbar during 3 hours. Residual methanol was  
10 distilled off during this time. When distillation had ceased, the reaction mixture was cooled to room temperature. The light yellow oily product is analyzed by infrared spectroscopy. There was no hydroxyl signal at 3400  $\text{cm}^{-1}$  visible in the infrared spectrum. The yield was 914 g.

15 C: Preparation of the BOE derivative of di-3-ethyloxetan-3-yl methyl ester of dimer fatty acid (BOE 4)

In a flask equipped as in Example 7A were weighed di-3-ethyloxetan-3-yl methyl ester of dimer fatty acid prepared as specified in Example 7B (914 g) and butyl acetate (1400 g). At room temperature  $\text{BF}_3\text{-Et}_2\text{O}$  (9,15 g) was  
20 added thereto during 15 minutes. The reaction mixture was heated to 50°C and kept at that temperature for 10 hours. Next, the reaction mixture was cooled to room temperature and 6,5 g triethyl amine was added. A precipitate was formed, which was filtered off. The product analyzed by infrared spectroscopy showed a small signal at 3400  $\text{cm}^{-1}$  indicating  
25 hydroxyl functionality. Phenyl isocyanate (9 g) was added to the product. After 1 hour at room temperature infrared spectroscopy indicated the absence of hydroxyl functionality (no signal at 3400  $\text{cm}^{-1}$ ) and of isocyanate functionality (no signal at 2270  $\text{cm}^{-1}$ ). Part of the butyl acetate was

evaporated. The final product has a solids content of 82,7% and is a yellow oil.

#### Example 8

##### 5 A: Preparation of an oxetane-functional polyester

Diethyl malonate (686,0 g, 4,3 moles), neopentylene glycol (358,1 g, 3,45 moles), 3-ethyl-3-hydroxymethyl oxetane (196,2 g, 1,7 moles), dibutyl tin oxide (1,2 g), and xylene (100 g) were weighed into a 2 l three-neck flask equipped with a distilling set-up. The reaction mixture was heated to reflux  
10 temperature. At 189°C the ethanol distillation began. The distillation speed was controlled by slowly increasing the reaction temperature. At a temperature of 210°C all ethanol had been distilled off. The xylene was removed from the reaction mixture under reduced pressure. The obtained oxetane-functional polyester had a molecular weight of  $M_n=1021$  and  
15  $M_w=1875$  (GPC, polystyrene standard).

##### B: Preparation of a BOE-functional polyester

This reaction was carried out under a nitrogen atmosphere. Into a round-bottomed flask were weighed: the oxetane-functional polyester as prepared  
20 in Example 8A (800,0 g, 1,6 equivalents of oxetane) and  $\text{BF}_3\text{Et}_2\text{O}$  (about 1 g). An exothermic reaction took place. The temperature of the reaction mixture rose to 62°C. Next, there was cooling with a water bath. After one night virtually all oxetane groups were found to have been converted into the corresponding BOE groups (BOE signal at  $\delta$  (ppm) 4,0 in  $^1\text{H}$  NMR). The  
25 obtained BOE-functional polyester had a molecular weight of  $M_n=1648$  and  $M_w=7449$  (GPC, polystyrene standard).

Example 9A: Preparation of 3-ethyloxetan-3-yl methyl acrylate

The synthesis was carried out as described by P.G. Gassman et al., Chem. Comm., (1989), p. 837.

5

The reaction was carried out under a nitrogen atmosphere. To a mixture of 3-ethyl-3-hydroxymethyl oxetane (170,6 g, 1,50 moles) and triethyl amine (153,8 g, 1,52 moles) in tetrahydrofuran (500 g) cooled in an ice bath acryloyl chloride (137,5 g, 1,52 moles) was added dropwise. The reaction mixture was stirred for one hour at room temperature. To the reaction mixture 500 g of water were added. The organic layer was separated from the aqueous layer. The aqueous layer was extracted with diethyl ether (2 x 500 ml). The combined organic layers were dried with a saturated NaCl solution and magnesium sulphate. Following filtration of the ether layer the volatile organic compounds were removed under vacuum using a rotary vacuum evaporator. The residue was distilled under vacuum. 3-ethyloxetan-3-yl methyl acrylate was isolated at 122°C/19 mbar as a clear oil. The yield was: 200,4 g, (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 0,92 (t, <sup>3</sup>H); 1,80 (q, <sup>2</sup>H); 4,30 (s, <sup>2</sup>H); 4,48 (dd, <sup>4</sup>H); 5,88 (d, <sup>1</sup>H); 6,18 (dd, <sup>1</sup>H); 6,45 (d, <sup>2</sup>H).

20

B: Preparation of a polyacrylate having BOE-functional side groups

A mixture of butyl acrylate (38,0 g), trimethyl cyclohexyl methacrylate (Nourycryl MC® 109, 45,0 g), 3-ethyloxetan-3-yl methyl acrylate (17,0 g), t-butylperoxy-3,5,5-trimethyl hexanoate (Trigonox® 42S, 3,0 g), and dodecyl mercaptan (2,0 g) was added over a period of 2 hours to refluxing MAK (42,7 g). During the feeding the temperature rose from 155°C to 169°C. After the feeding there were two further additions, each over 30 minutes, of

25



a solution of Trigonox® 42S (0,25 g) in MAK (1,0 g). The reaction mixture was cooled to room temperature. Next,  $\text{BF}_3\text{Et}_2\text{O}$  (0,75 g) was added. The obtained resin had the following physical properties:  $M_n=1736$ ,  $M_w=4567$ , viscosity = 1,28 Pa.s, and S.C.=74,7% (after 30 minutes of heating at 150°C).

#### Example 10 and Comparative Example A

##### BOE as main binder reacting with a polyisocyanate-containing compound

Desmodur® N3390 was mixed with (2,2-dimethylol-n-butyl)propionate (DBP) and BOE 2, respectively (130 eq.% NCO, calculated on (latent) hydroxyl). 0,15 wt.% of DBTL, calculated on solid matter, and 0,33 wt.% of PTSA, calculated on DBP, were added to the DBP mixture, while 0,15 wt.% of DBTL calculated on solid matter and 0,83 wt.% of PTSA calculated on BOE 2 were added to the BOE 2 mixture. The two mixtures were diluted with a 50:50 mixture of MAK/EAK to spraying viscosity ( $\pm$ DINC4 18"). 270 g of MAK/EAK were needed to give the DBP mixture the desired spraying viscosity. By contrast, the BOE 2 mixture required only 200 g. The use of BOE 2, in other words, makes for a 70 g reduction of the amount of diluent required to obtain a sprayable composition. The pot life and drying time data is compiled below. Pot life is defined as the time during which the viscosity of the coating composition increased to 30" DINC4. The coating compositions were sprayed on a steel plate to obtain a 50 $\mu$  layer after drying. It is obvious that the coating composition according to the present invention has a longer pot life and a shorter drying time, in other words, an especially favourable pot life:drying time ratio.

Example		Pot life	Drying time (min.)
A	DBP	10 min.	140
9	BOE 2	> 1 day	100

Example 11 and Comparative Example BSOE as main binder reacting with a polyisocyanate-containing compound

- 5 Two samples of SOE 2 were mixed with Desmodur® N3390 (130 eq.% of NCO, calculated on latent hydroxyl), 0,3 wt.% of DBTL, calculated on solid matter, was added to the two mixtures, while 1,1 wt.% of PTSA, calculated on SOE 2, was added to one of the mixtures. The coating compositions were applied on a steel plate with a 100 $\mu$  draw bar. The S.C. results are
- 10 compiled below. They clearly show the effect PTSA has on the deblocking of the hydroxyl groups in the SOE composition.

Example	PTSA	S.C.	
		max. theoretical	measured
11	1,1 wt. %	83,6%	80,4%
B	-	83,6%	59,1%

15

Examples 12-18BOE as main binder reacting with a polyisocyanate-containing compound

- 4,3 parts by weight of BOE 2 were mixed with 10,8 parts by weight of Desmodur ® N3390 (100 eq.% NCO, calculated on latent hydroxyl). 0,3
- 20 wt.% of DBTL, calculated on solid matter, was added. Various acids were added as catalysts for the hydrolysis of the BOE compound. The coating compositions were applied on steel plates with a 100 $\mu$  draw bar. The data is compiled below. The percentages of catalyst mentioned in the table are based on the amount of BOE 2. PTSA has a pKa of 0,5-1, the pKa of
- 25 benzoic acid (BZ) is 4,2, and the pKa of DBF is 2-3. The S.C. is measured after 1 day drying at room temperature and 1 hour at 120°C.

Example	Cat. (%)	S.C. film	Max. S.C. theor.	Min. S.C. theor.	Gelling time	Touch dry time
12	-	72,2	93,2	62,6	>1 week	3 hrs.
13	1,63 ZnCl <sub>2</sub>	64,3	92,4	60,6	>1 week	1 hr.
14	1,63 BZ	70,2	89,2	56,6	>1 week	2 hrs.
15	0,47 PTSA	71,4	92,4	62,0	>1 week	4 hrs.
16	1,63 PTSA	89,4	92,4	60,6	>1 week	3 hrs.
17	1,63 BF <sub>3</sub> Et <sub>2</sub> O	87,5	92,4	60,6	>1 week	>4 hrs.
18	1,63 DBP	88,0	92,4	60,6	>1 week	>5 hrs.

5

In all cases there is excellent pot life. The S.C. improves with the use of stronger acid or larger quantities of acid. Example 16 provides the best results with a high S.C. and a reasonable drying time.

#### 10 Comparative Examples C and D

Example 12 was repeated. Instead of 4,3 parts of BOE 2, 3,7 parts of 2-ethyl-1,3-hexane diol were added. Two mixtures were prepared comprising 0,005 parts by weight and 0,05 parts by weight of DBTL, calculated on solid matter, respectively. For the first mixture a pot life of 0,5 hour was measured, for the second, one of 1 minute. The touch dry time of the coating composition when using 0,05 parts by weight of DBTL was over 4 hours at room temperature.

15

Example 19 and Comparative Example EBOE as reactive diluent in a composition comprising a polyester polyol and a polyisocyanate-functional compound

The diluting capacity of BOE 2 was compared with ethylbutyl propane diol (EBP), a hydroxyl-functional compound, in a high solids urethane coating formulation. Use was made of 130 eq.% NCO (Desmodur® N3390) on (latent) hydroxyl. Polyester polyol A was used as the binder. The catalyst used for the BOE hydrolysis was PTSA, the catalyst for the isocyanate-hydroxyl reaction was DBTL. It can be seen from the table that when BOE 2 is used, there is 65 grams less solvent present per kilogram of paint (about 65 grams per liter). Because of the lower equivalent weight of BOE 2 in comparison with EBP, comparatively speaking a little more isocyanate is needed for cross-linking. All amounts are in parts by weight.

	Example E	Example 19
Polyester A	40	40
BOE 2	-	8,1
EBP	8,1	-
Desmodur® N3390	54,4	61,9
DBTL	0,12	0,06
PTSA	-	0,4 (4,9 wt.% calc. on BOE 2)
MAK	30,8	26,3
EAK	16	9,5
Shellsol D	7,34	8,4
Viscosity (DINC4)	18,2"	17,6"

15

20

Example 20 and Comparative Example FBOE as main binder with a polyisocyanate-functional compound

The performance of BOE 2 was compared with that of a commercially available reactive diluent, Oxazolidine Zoldine® RD 20 ex. Angus Chemical  
5 Company (1-aza-3,7-dioxo-bicyclo-2,8-diisopropyl-5-ethyl-[3,3,0]-octane).

Desmodur® N3390 was cross-linked with the two compounds (130 Eq. % NCO, calculated on (latent) hydroxyl). The coating compositions were diluted with MAK:EAK (50:50) to a viscosity of 19" DINC4. Added were 0,1  
10 wt.% of DBTL, calculated on solid matter, and 0,57 wt.% of PTSA, calculated on BOE 2. Both compositions were sprayed onto bare steel. The temperature during drying was 20°C, the relative humidity 70%. Below it can be seen that the pot life is longer when use is made of BOE 2, while drying proceeds more rapidly.

15

Example		Viscosity after 6 hrs. (DINC4)	Drying (min.)
20	: BOE 2	23"	175
F	: Zoldine®	29"	400

20

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Examples 21 and 22 and comparative Example G

BOE as main binder in combination with a polyisocyanate-functional compound and an acid generating initiator.

A coating composition was prepared containing

- 5     5,3 parts by weight of BOE 3B  
      10,8 parts by weight of Desmodur® N3390  
      1,5 parts by weight of 10% DBTL in butylacetate  
      1,06 parts by weight of 20% 2-methyl-1-[4-(methylthio)phenyl]-2-[4-methylphenylsulphonyl] propan-1-one (MDTA), ex. Fratelli Lamberti Spa,  
10 Varese, Italy, in butyl acetate.

- The coating composition was applied with a draw bar onto two steel plates to give a 50 µm film thickness after drying. Five minutes after application one steel plate was irradiated by UV-A for 1 minute (Example 21). After an  
15 hour at room temperature the coating was touch dry and clear. The unirradiated coating (comparative example G) was touch dry after 5 hours but was very troubled due to unhydrolysed BOE. The coating composition was stored for a week at 50°C. Then it was applied as described above (example 22). The coating was again touch dry after an hour. The storage  
20 stability of the MDTA containing coating composition is very good.

Example 23 and Comparative Example H

BOE as main binder with a polyacetal-functional resin

- 25 Two coating compositions were prepared as listed below (all amounts in parts by weight). The polyacetal-functional resin is a copolymer of glycerol cyclocarbonate methacrylate and styrene, upon which amino butyraldehyde dimethyl acetal is adducted (S.C. = 62% in butyl acetate (wt. eq. acetale

groups = 951)). BOE 4 has a S.C. of 83% in butylacetate, the wt. eq. BOE = 476). Nacure was diluted to a 10% solution in butyl acetate.

As can be seen from the results listed below the composition of the present invention has an excellent potlife. The coating compositions were applied with a draw bar onto a steel plate to give a 50  $\mu$ m film thickness after drying. The touch dry time of the coating composition of the present invention is equal to the comparative coating composition as well as the solvent resistance to MEK.

10

	Example 23	Comparative Example H
polyacetal-functional resin	9,5	9,5
BOE 4	4,8	—
Hydrolysed BOE 4	—	4,8
10% Nacure 5076	1,0	1,0
gel time in the pot	> 2 weeks	5 hours
Touch dry time	10 minutes	10 minutes
MEK resistance after 1 week	2	2

Example 24 and Comparative Example I  
BOE as main binder with polyalkoxysilane-functional resin

15

Two coating compositions were prepared as listed below (all amounts in parts by weight). The polyalkoxysilane-functional resin is an adduct of 1 mole of diethyl malonate and 2 moles of 3-amino propyl trimethoxy silane, i.e. AMEO-T ex. Wacker (S.C. = 95,6% in xylene (wt. eq.  $\text{Si}(\text{EtO})_3$  groups =

255)). BOE 4 has a S.C. of 83% in butylacetate, the wt. eq. BOE = 476).  
Nacure 5076 was diluted to a 10% solution in butyl acetate.

As can be seen from the results listed below the composition of the present  
5 invention has an excellent potlife. The coating compositions were applied  
with a draw bar onto a steel plate to give a 50 µm film thickness after  
drying. The touch dry time of the coating composition of the present  
invention is equal to the comparative coating composition as well as the  
solvent resistance to MEK.

10

	Example 24	Comparative Example I
polyalkoxysiloxane-functional resin	5,1	5,1
BOE 4	4,8	—
Hydrolysed BOE 4	—	4,8
10% Nacure 5076	0,9	0,9
gel time in the pot	> 2 weeks	1 hours
Touch dry time	20 minutes	20 minutes
MEK resistance after 1 week	2	2

#### Example 25

BOE as main binder with a melamine resin

15

A coating compositions was prepared as listed below (all amounts in parts  
by weight).



Example 25	
Resimene RF 4518	8
BOE 3B	2
Nacure 5076	0,6
gel time in the pot	< 1 hour
Touch dry time	1,5 hours
MEK resistance after 1 week	2

- The results listed above show that a composition comprising a melamine resin and a catalyst frees water which result in a very quick ring opening of the BOE compound. Accordingly, the potlife is very short and this coating
- 5 composition asks for a 2K component system or a blocked catalyst. The coating composition was applied with a draw bar onto a steel plate to give a 50  $\mu\text{m}$  film thickness after drying.

#### 10 Examples 26 and 27

##### Solvent free clearcoat compositions

- Two solvent free clearcoat compositions were prepared as listed below. The coatings were made according to a 3 pack system. The first component contained the BOE compound, the second component
- 15 contained the polyisocyanate compound and the third component contained the acid catalyst. Solvent-free is defined as  $\text{VOC} < 100 \text{ g/l}$ .

Component	Compound	Example 26	Example 27
1	BOE 3B	34.2 g	30.2 g
	Caster oil	—	6.0 g
	DBTL	0.51 g	0.54 g
	Byk 333	0.41 g	0.44 g
2	Desmodur <sup>®</sup> N3400	63.5 g	46.5 g
	Desmodur <sup>®</sup> VL50	-	14.8 g
3	Nacure 5076	1.37 g	1.45 g

Both compositions have a viscosity of 23" (DINC4). The clearcoats were sprayed on steel panels coated with Autobase MM-basecoat, ex. Sikkens, with a high volume low pressure spraygun (HVLP). The coatings were cured at room temperature and 60°C. Appearance was excellent, good gloss, and good flow/leveling. Stone chip resistance, solvent resistance and adhesion were good.

#### 10 Examples 28 and 29

##### Solid color topcoat compositions

Two solid color topcoat compositions were made based on BOE. In the first composition the pigment was dispersed in BOE, while in the second composition a pigment paste based on polyester is used. Component 1 was milled on a bead mill until the particle size was smaller than 10  $\mu$ .

Component	Compound	Example 28	Example 29
1	BOE 3B	37.5 g	---
	polyester polyol B	---	45.0 g
	Irgazin DPP Red BO	33.6 g	24.7 g
	Disperbyk 166	16.8 g	17.0 g
	Butylacetate	6.1 g	6.6 g
	Solvesso 100	6.1 g	6.6 g
2	BOE 3B	34.8 g	28 g
	Desmodur® N3390	141.4 g	80 g
	DBTL	1.08 g	0.96 g
3	Nacure 5076	1.44 g	0.56 g
	Solvesso 100	17.0 g	4.0 g
	Ethoxyethyl propionate	17.0 g	4.0 g

Both coating compositions were sprayed on steel panels prepared with a conventional primer as a car refinish topcoat. Appearance and application behavior is good. The VOC level is at a very low level, approximately 250 g/l.

#### Examples 30 and 31

##### Clearcoat coating compositions

- 10 Two clearcoat coating compositions were prepared as listed below. Both coating compositions have a viscosity of 16" DIN4. Potlife of the coating composition of Example 30 is shorter than the potlife of the coating composition of Example 31, due to the presence of hydroxyl-functional

polymer in BOE 3A. Both clearcoat compositions were sprayed on steel panels prepared with Autobase MM basecoat, ex. Sikkens, using a HVLP spraygun. Room temperature cure of the coating composition of Example 30 is faster than the cure of the coating composition of Example 31.

- 5 Appearance and gloss of both coatings are excellent.

Component	Compound	Example 30	example 31
1	BOE 3A	40 g	-
	BOE 3B	-	40 g
	DBTL (10% in butylacetate/ xylene (1/1))	4 g	4 g
	Byk 322, Byk 355, butylacetate (20/15/65)	2 g	2 g
	Solvesso 100/ ethoxyethyl propionate (1/1)	14 g	24 g
2	Desmodur <sup>®</sup> N3390	67.6 g	78.5 g
3	Nacure 5076	1.14 g	1.14 g

10 Examples 32 and 33

Clearcoat coating compositions

Two clearcoat coating compositions were prepared as listed below. Both clearcoat compositions were sprayed on steel panels prepared with Autobase MM basecoat, ex. Sikkens, using a HVLP spraygun. Both

clearcoats have excellent paint properties. Application properties are very good. Appearance and gloss are excellent.

5

Component	Compound	Example 32	Example 33
1	BOE 3B	34 g	34 g
	polyester polyol B	7.5 g	—
	polyester polyol C	—	7.5 g
	DBTL (10% in butylacetate/ xylene (1/1))	4.0 g	4.0 g
	Byk 322, Byk 355, butylacetate (20/15/65)	8.56 g	8.56 g
	Solvesso 100	5.6 g	5.6 g
	Ethoxyethyl propionate	5.6 g	5.6 g
	Tinuvin 1130	0.1 g	0.1 g
	Tinuvin 123	0.05 g	0.05 g
2	Desmodur <sup>®</sup> N3390	71.0 g	71.0 g
3	Nacure 5076	0.98 g	0.98 g

#### Examples 34 and 35

#### Primer compositions

- 10 Two ultra high solid primer compositions were prepared as listed below. Component 1 was stirred at high speed for 15 minutes and subsequently

passed twice through a closed mill to obtain a fineness of less than 25  $\mu\text{m}$ .

Component 1 was then mixed with premixed components 2 and 3.

Component	Compound	Example 34	Example 35
1	BOE 3B	17,0 g	17,0 g
	Disperbyk 110	1,4 g	1,4 g
	Tioxide TR92	21,0	21,0
	Zinc phosphate ZP10	13,6	13,6
	Blank fix N	11,0	11,0
	China clay grade C	23,5	23,5
	Aerosil R972	0,8	0,8
	Solvesso 100	6,0	6,0
	Ethoxyethyl propionate	5,9	5,9
2	Fascat 4202	0,25	0,25
	Nacure 5076	0,35	0,35
	Byk 300	0,8	0,8
3	Desmodur <sup>®</sup> L75	—	23,4
	Vestanat <sup>®</sup> T1890E	25,1	—
	Desmodur <sup>®</sup> LS 2025	25,1	25,1
	Butyl acetate	4,0	4,3
	Solvesso 100	7,0	7,5

Both primer coating compositions were applied with conventional spray equipment on steel panels and had a spray viscosity around 2.0 Poise (measured with a Sheen Rotothinner) at a VOC around 290 g/l. Dried at

room temperature (overnight) or at 60°C (30 minutes), hard and good sandable coatings were obtained which can be topcoated with regular carrefinish topcoat systems and/or coating compositions of the present invention such as exemplified in Examples 26-29 (pigmented topcoats as well as base/clear systems).

Advantages over existing Medium Solid 2k primer/filler materials as used in the carrefinish market nowadays are: a very low VOC, a long potlife and a high build behavior. Compared to existing High Solids primer compositions comprising imine crosslinkers advantages are again a long potlife, fast drying at 60°C, and the fact that there is no emission of volatile blocking components (like aldehydes and ketones from crosslinkers such as ketimines, aldimines and oxazolidines).

Examples 36, 37, and 38 and Comparative Example J

BOE 3B as reactive diluent in a clearcoat coating composition

A commercial available clearcoat component Sikkens Autoclear MS 2000 was diluted with different amounts of BOE 3B. Compositions are listed below. Component 1 was mixed with components 2 and 3 and sprayed on steel panels prepared with Autobase MM basecoat, ex. Sikkens, using a HVLP spraygun.

Component	Compound	C. Ex. J	Ex. 36	Ex. 37	Ex. 38
1	MS 2000	100	100	100	100
	BOE 3B		4,4	11,1	17,8
	DBTL		0,2	0,9	1,6
	Acetyl acetone		0,3	1,1	1,9
	Nacure 5076		0,1	0,3	0,5
2	Hardener MS Standard	50			
	Desmodur® N3390		32,6	43,1	53,6
3	1.2.3. Thinner slow	9,4	33	35	35

Properties	C. Ex. J	Ex. 36	Ex. 37	Ex. 38
VOC (g/l)	560	529	498	468
Viscosity (DINC4, sec.)	18	18	19	19
ratio NCO/OH	78	100	100	100
Touch dry (60°C, min.)	30	10	10	10
Touch dry (RT, min.)	120	120	77	60
Potlife (min.)	>180	60	60	60
Gloss	74	86	82	83

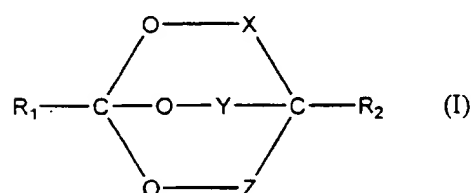
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The addition of BOE 3B as a reactive diluent results in a VOC reduction, a decrease in drying time, and an increase in gloss.



# Claims

1. A coating composition comprising a first compound comprising at least one bicyclo-orthoester group or spiro-orthoester group, characterised in that the coating composition comprises a second compound comprising at least two hydroxyl-reactive groups.
2. A coating composition according to claim 1, characterised in that the bicyclo-orthoester group has a structure according to formula I



wherein

X and Z are independently from each other selected from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

Y is nothing or is selected independently of X and Z from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

R<sub>1</sub> and R<sub>2</sub> may be the same or different and are selected from the group of monovalent radicals comprising

hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea,

urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and

divalent radicals comprising

alk(en)ylene groups having 1-10 carbon atoms which groups may be

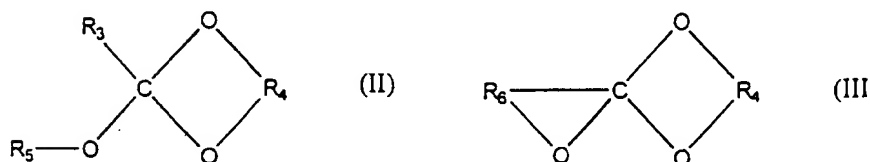
5 linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphonyl, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphonyl, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, ester groups; ether groups; amide groups; thioester groups; thioamide groups; urethane groups; urea groups; and a single bond.

15 3. A coating composition according to claim 2, characterised in that X, Y, and Z are methylene.

4. A coating composition according to one or more of claims 2 and 3, characterised in that in the case of monovalent radicals  $R_1$  and  $R_2$  are independently from each other selected from the group of hydrogen, hydroxyl, and linear or branched alk(en)yl groups having 1-20 carbon atoms, optionally substituted with one or more hydroxyl groups and optionally containing an ester group.

25 5. A coating composition according to claim 4, characterised in that  $R_1$  and  $R_2$  are independently from each other selected from the group of methyl, methylol, ethyl, ethylol, propyl, propylol, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and a  $-CH_2 - CH_2 - O - CO - C_{1-20}$  alk(en)yl group.

6. A coating composition according to claim 2, characterised in that one or both  $R_1$  and  $R_2$  groups is a divalent radical, with the first compound being a polymer comprising at least one bicyclo-orthoester group.
7. A coating composition according to claim 6, characterised in that one or both  $R_1$  and  $R_2$  groups are selected from the group of ester, ether, urethane, a single bond, and linear or branched alk(en)ylene groups having 1-10 carbon atoms optionally containing one or more ester, ether or urethane groups.
8. A coating composition according to claim 1, characterised in that the spiro-orthoester group has a structure according to formula II or III



wherein

- 20  $R_3$  and  $R_5$  are independently from each other selected from the group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and

$R_4$  and  $R_6$  are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and divalent radicals such as a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.

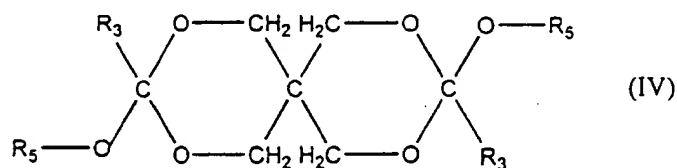
9. A coating composition according to claim 8, characterised in that  $R_3$  and  $R_5$  are independently from each other selected from linear or branched alk(en)yl groups having 1-4 carbon atoms.
10. A coating composition according to one or more of claims 8 and 9, characterised in that  $R_4$  is ethylene optionally substituted with a linear or branched alkyl group having 1-5 carbon atoms, optionally containing one or more oxygen and nitrogen atoms.
11. A coating composition according to claim 10, characterised in that  $R_4$  is



12. A coating composition according to one or more of claims 8, 9, 10 or 11, characterised in that  $R_6$  is propylene.

13. A coating composition according to one or more of claims 8 and 9, characterised in that the first compound is a spiro-orthoester-functional compound according to formula IV

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wherein  $R_3$  and  $R_5$  are independently from each other selected from linear or branched alk(en)yl groups having 1-4 carbon atoms.

10

14. A coating composition according to one or more of claims 8 and 9, characterised in that one or both  $R_4$  and  $R_6$  groups is substituted with a divalent radical, with the first compound being a polymer comprising at least one spiro-orthoester group.

15

15. A coating composition according to one or more of the preceding claims, characterised in that the second compound comprises at least two hydroxyl-reactive groups selected from the group of isocyanate groups, epoxy groups, acetal groups, carboxyl groups, anhydride groups, and alkoxy silane groups, or the second compound is an amino resin.

20

16. A coating composition according to claim 15, characterised in that the hydroxyl-reactive compound is an aliphatic, alicyclic or aromatic compound comprising at least two isocyanate groups or adducts thereof.

25

17. A coating composition according to claim 16, characterised in that the second compound is selected from the group of biurets, isocyanurates, allophanates, uretdiones, and mixtures thereof.
- 5 18. A coating composition according to one or more of the preceding claims, characterised in that the coating composition contains additionally at least one compound selected from the group of hydroxyl-functional binders, hydroxyl-functional oligomers and monomers, ketone resins, aspartyl acid esters, and latent or non-
- 10 latent amino-functional compounds.
19. A coating composition according to claim 18, characterised in that the hydroxyl-functional binders are selected from polyester polyols, polyether polyols, polyacrylate polyols, polyurethane polyols,
- 15 cellulose acetobutyrate, hydroxyl-functional epoxy resins, alkyds, and dendrimeric polyols.
20. A process for curing a coating composition according to one or more of the preceding claims, characterised in that the latent hydroxyl
- 20 groups of the bicyclo-orthoester groups or spiro-orthoester groups are deblocked in the presence of water, optionally in the presence of a first catalyst, and reacted with the hydroxyl-reactive groups of the second compound, optionally in the presence of a second catalyst.
- 25 21. A process according to claim 20, characterised in that the first catalyst is selected from the group of Lewis acids and Brønsted acids.
22. A process according to claim 21, characterised in that the Lewis acid
- 30 is  $\text{BF}_3\text{Et}_2\text{O}$ .

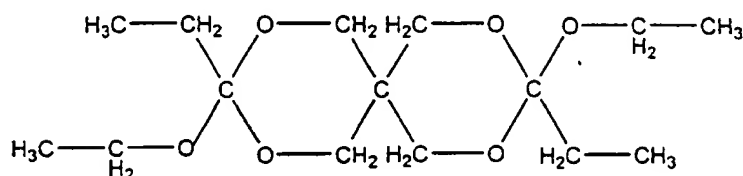
23. A process according to claim 22, characterised in that the Brønsted acid has a  $pK_a < 3$ .
- 5 24. A process according to claim 23, characterised in that the Brønsted acid is selected from the group of a mono- or dialkyl phosphate, a carboxylic acid having at least one chlorine and/or fluorine atom, an alkyl or aryl sulphonic acid or an (alkyl)phosphoric acid.
- 10 25. A process according to claim 24, characterised in that the Brønsted acid is selected from the group of methane sulphonic acid, paratoluene sulphonic acid, optionally substituted naphthalene sulphonic acids, dodecyl benzene sulphonic acid, dibutyl phosphate, trichloroacetic acid, phosphoric acid, and mixtures thereof
- 15 26. A process according to one or more of claims 20-25, characterised in that use is made of 0 to 10 wt.% of the first catalyst, calculated on BOE-functional and SOE-functional compounds.
- 20 27. A process according to claim 26, characterised in that use is made of 0,3 to 8 wt.% of first catalyst.
- 25 28. A process according to one or more of claims 20-27, characterised in that the second catalyst is selected from the group of dimethyl tin dilaurate, dibutyl tin dilaurate, dibutyl tin diacetate, tin octoate, zinc octoate, aluminum chelate, dimethyl tin dichloride, tertiary amines, Lewis acids such as  $BF_3$  or organic complexes thereof, paratoluene sulphonic acid, dodecyl benzene sulphonic acid, phosphoric acid, and mixtures thereof.

29. A process according to claim 28, characterised in that the second catalyst is present in an amount of 0,001 to 5 wt.%, calculated on solid matter.
- 5 30. A two-component system, characterised in that one component comprises at least one bicyclo- or spiro-orthoester compound and at least one hydroxyl-reactive compound and the second component comprises a first catalyst for the hydrolysis of the bicyclo- or spiro-orthoester compound.
- 10 31. A three-component system, characterised in that one component comprises at least one bicyclo- or spiro-orthoester compound, a second component comprises at least one hydroxyl-reactive compound, and a third component comprises a first catalyst for the hydrolysis of the bicyclo- or spiro-orthoester compound.
- 15 32. A process for the preparation of a compound comprising at least one bicyclo-orthoester group in which a compound having at least one corresponding oxetane group is converted in the presence of a catalytic amount of a strong Brønsted or Lewis acid or organic complexes thereof.
- 20 33. A process according to claim 32, characterised in that the Lewis acid is  $\text{BF}_3\text{Et}_2\text{O}$ ,  $\text{BF}_3\cdot 2\text{CH}_3\text{COOH}$ , and  $\text{SnCl}_4$ .
- 25 34. A process according to one or more of claims 32 and 33, characterised in that the catalyst is employed in amounts of 0,001-0,1 mole of catalyst per mole of oxetane group.



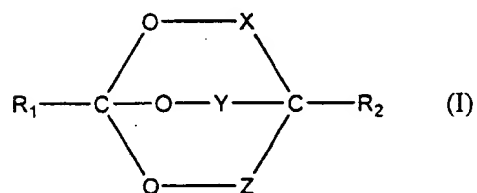
35. A process according to one or more of claims 32-34, characterised in that the reaction takes place in the presence of a small amount of solvent, preferably without solvent.

- 5 36. A process for the preparation of



- characterised in that pentaerythritol is reacted with triethyl  
10 orthopropionate in the presence of paratoluene sulphonic acid, with  
trimethyl benzene being used as solvent.

37. A polymer comprising at least one bicyclo-orthoester group according to formula I



wherein

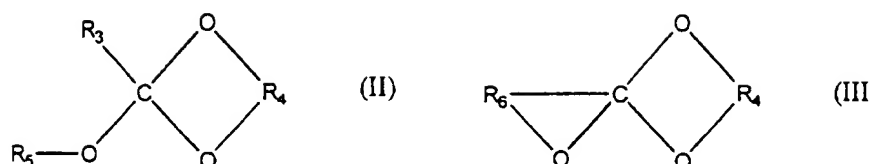
- 20 X and Z are independently from each other selected from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;  
Y is nothing or is selected independently of X and Z from linear or branched alk(en)ylene groups with 1-4 carbon atoms optionally containing an oxygen or a nitrogen atom;

one of  $R_1$  and  $R_2$  is a monovalent radical and the other is a divalent radical or both groups are independently from each other selected from the group of divalent radicals, the monovalent radicals comprising

5 hydrogen, hydroxyl, alk(en)yl groups comprising 1-30 carbon atoms which may be linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphony, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and acyl groups, and

divalent radicals comprising  
alk(en)ylene groups having 1-10 carbon atoms which groups may be  
15 linear or branched and may optionally contain one or more heteroatoms and groups selected from the group of oxygen, nitrogen, sulphur, phosphorus, sulphone, sulphony, and ester, optionally substituted with epoxy, cyano, amino, thiol, hydroxyl, halogen, nitro, phosphorus, sulphony, amido, ether, ester, urea, urethane, thioester, thioamide, amide, carboxyl, carbonyl, aryl, and  
20 acyl groups, ester groups; ether groups; amide groups; thioester groups; thioamide groups; urethane groups; urea groups; and a single bond.

25 38. A polymer comprising at least one spiro-orthoester group according to formula II or III



wherein

- 5         $R_3$  and  $R_5$  are independently from each other selected from the group of linear or branched alk(en)yl, aryl or acyl optionally containing one or more oxygen, nitrogen, sulphur or phosphorus atoms, optionally substituted with a halogen atom; and
- 10         $R_4$  and  $R_6$  are independently from each other selected from an alkylene group having 1-3 carbon atoms optionally substituted with one or more groups selected from monovalent radicals such as linear or branched alk(en)yl, aryl or acyl groups optionally containing one or more oxygen, nitrogen, sulphur, and phosphorus atoms; and at least once substituted with a divalent radical selected
- 15        from the group of a single bond and an alkylene group having 1-10 carbon atoms with or without one or more atoms and groups selected from oxygen, nitrogen, sulphur, and phosphorus atoms, and ether, ester, and urethane groups.
- 20    39. A polymer according to either of claims 36 and 37, characterised in that the polymer is a polyacrylate or a polyester.

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/EP 97/00892

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09D175/04 C07D493/08 C07D493/10 C08F8/14 C08G18/30  
C08G63/91 C09D201/06 C08G85/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G C08F C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 31 28 217 A (TOA GOSEI CHEM IND) 13 May 1982 see claims 1,2,4 see page 8, line 15 - line 32 see page 24, line 34 - page 28, line 23 ---	1-4, 15-19
X	DATABASE WPI Week 8443 Derwent Publications Ltd., London, GB; AN 84-267189 XP002016057 & JP 59 164 334 A (TOA GOSEI) , 17 September 1984 see abstract --- -/-	1-10,15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

10 June 1997

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No.

PC1/EP 97/00892

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	<p>EP 0 575 667 A (THE PROCTER &amp; GAMBLE CO.)  29 December 1993  see claims 9-13</p> <p>---</p>	38,39
X	<p>DATABASE WPI  Week 8350  Derwent Publications Ltd., London, GB;  AN 83-841276  XP002016059  &amp; JP 58 189 211 A (TOA GOSEI) , 4 November  1983  see abstract</p> <p>---</p>	38,39
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A	<p>DE 15 95 673 A (BAYER) 18 September 1969  see claim 1  see page 4, paragraph 2  see page 6, paragraph 2 - page 7,  paragraph 2</p> <p>-----</p>	1

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Information on patent family members

International Application No

PCT/EP 97/00892

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